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TITLE:	**SCANNING PROBE MICROSCOPY TIPS COMPOSED OF NANOPARTICLES AND METHODS TO FORM SAME**
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SCANNING PROBE MICROSCOPY TIPS COMPOSED OF NANOPARTICLES AND METHODS TO FORM SAME

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention generally relates to scanning probe microscopy (SPM) and more particularly to a scanning probe microscope tip with improved spatial resolution using chemically-synthesized nanoparticles.

Description of the Related Art

[0002] In scanning probe microscopy, specimens are imaged by scanning a sharp probe tip in close proximity to the specimen surface. Data acquired from the probe tip is plotted as a function of the location of the probe tip in the plane of the specimen surface.

[0003] Magnetic force microscopy is one of numerous scanning probe microscopy (SPM) techniques. Magnetic force microscopy is a probe to image magnetic fields in magnetic thin films. In the past, spatial resolution of magnetic details of approximately 10 nm has been achieved Therefore, using a magnetic force microscope (MFM) is an effective tool to measure small magnetic fields arising from submicrometer scaled features.

[0004] The class of scanning probe microscopes further includes scanning tunneling microscopes (STM), near-field scanning optical microscopes (NSOM), scanning electrochemical microscopes (SECM) and atomic force microscopes (AFM). AFMs can observe the surface configuration of an insulating sample on an atomic scale.

[0005] The MFM consists of an AFM with a probe that contains a magnetic material. In a typical MFM system, a sharp magnetic tip is mounted on a cantilever force sensor. The tip is placed over a magnetic specimen at a separation of 10 nm to 500 nm from the surface of the specimen. Piezoelectric elements, capable of producing displacements as small as 0.01 nm, are used for positional control of the tip or specimen in any direction. The magnetic forces that act on the probe tip from the specimen cause a static deflection of the cantilever. This deflection is monitored by use of a laser detection system, for example, whereby the static deflection of the cantilever causes a corresponding displacement of a reflected laser light beam.

[0006] The scanning probe microscopy image is a composite of the effects of all the forces acting on the probe tip. In the absence of other field gradients, long-range Van der Waals forces attract the probe tip to the specimen surface and can be used to generate a topographic image of the surface of the specimen. Moreover, magnetic field gradients can be imaged if the probe tip has a sufficient magnetic dipole moment. The image may show only the magnetic field effects, a superposition of magnetic and topographic effects, or only topography, depending on the relative strength of the magnetic field and Van der Waals gradients as well as the material characteristics of the magnetic probe tip

[0007] The material properties of the probe tip contribute to the increase or decrease in spatial resolution of an MFM. Various materials have been used for the magnetic probe tip in

MFM. For example, use of a magnetized iron tip is described by Martin et al., "High-resolution Magnetic Imaging of Domains in TbFe by Force Microscopy", Appl Phys. Lett , Vol. 52, No. 3, Jan. 18, 1988, pp. 244-246. Also, the use of silicon tips coated with a film of magnetic material, such as NiFe or CoPtCr, in MFM is described by Grutter et al., "Magnetic Force Microscopy with Batch-fabricated Force Sensors", J. Appl. Phys., Vol. 69, No. 8, Apr. 15, 1991, pp. 5883-5885. The standard method for forming an MFM sensor is to coat a standard AFM tip with magnetic material using standard thin-film deposition methods such as evaporation or sputtering. MFM sensors fabricated in this manner are limited in resolution by two main factors: 1) the film thickness of the magnetic coating layer increases the tip radius-of-curvature, thus decreasing resolution; and 2) the size of the magnetic domains in such a continuous thin-film also limits the resolution. Various methods have been attempted in an effort to overcome these problems. Patterning of the magnetic film deposited on the AFM tip can be done by ion-milling (S. H. Liou, IEEE Transactions on Magnetics, 35, 3989 (1999)). Alternatively, electron-beam lithography combined with shadow-evaporation of thin-films can produce regions of magnetic materials confined to the tip apex (G. D. Skidmore and E. D. Dahlberg, *Applied Physics Letters* 71, 3295 (1997), S. Y. Chou, S. Wei., P. Fischer, *IEEE Transactions on Magnetics* 30, 4485, (1994), M. Ruhrig et al., *J. Appl. Phys.* 79, 2913 (1996)). Both of these techniques are quite labor-intensive and are difficult to implement in a parallel manner.

[0008] Nanoparticles with diameters ranging from 2 nm to 20 nm can be made out of a wide variety of organic and inorganic materials (C. B. Murray, D. J. Norris, M. G. Bawendi, *J. Am. Chem. Soc.* 115, 8706 (1993), L. Brus in "Materials Chemistry: An Energy Discipline," G A Ozin ed., 335 (ACS Sympos. Ser. No. 245, 1995)). Nanocrystals are a subclass of nanoparticles

composed of well-characterized, crystalline cores and thin organic coats. Nanocrystals are monodisperse in terms of their size, internal structure (lattice), surface chemistry, and shape. Nanoparticles dispersed in liquids and nanoparticles deposited on solid substrates have provided much information on the submicroscopic properties of materials (A. P. Alivisatos, *Science* 271, 933 (1996)). Nanoparticles, and more specifically nanocrystals, attached to SPM tips could provide probes sensitive to a wide range of physical and chemical properties of a specimen, on a nanometer length-scale.

[0009] However, nanoparticles have not been used in SPM before because there did not exist a good method for attaching nanoparticles to SPM tips. Furthermore, magnetic nanoparticles have not been used in MFM before because, until recently, high-quality magnetic nanoparticles were unavailable (S. H. Sun, C. B. Murray, D. Weller, L. Folks, A. Moser, *Science* 287, 1989 (2000)). Thus, there is a need for an improvement in the spatial resolution of a scanning probe microscope using a new material composition for constructing the probe tip.

SUMMARY OF THE INVENTION

[0010] In view of the foregoing and other problems, disadvantages, and drawbacks of the conventional material compositions of the probe tips of scanning probe microscopes, the present invention has been devised, and it is an object of the present invention to provide a structure and method to improve the spatial resolution of a scanning probe microscope.

[0011] In order to attain the object suggested above, there is provided, according to one aspect of the invention a structure and method for improving the spatial resolution of a magnetic

force microscope (MFM) tip, which has been coated with a layer of chemically-synthesized nanoparticles The nanoparticles may be either single-species or heterogeneous, such that the single-species nanoparticles may be either ferromagnetic, paramagnetic, superparamagnetic, antiferromagnetic or ferrimagnetic. A heterogeneous coating may contain nanoparticles of one or more sizes and may comprise a mixture of one or more of the above-mentioned types of nanoparticles, or nanoparticles with one or more types of organic coats. The layer of nanoparticles is at least two nanoparticles thick, or alternatively, is a single layer of nanoparticles thick, or alternatively, is a single layer of nanoparticles thick and covers only the apex portion of the tip, or alternatively, only a single nanoparticle is affixed to the tip apex. Additionally, the layer of nanoparticles may be annealed at a high temperature to change the crystal structure of the nanoparticles, or to strengthen the adhesion of the nanoparticles to the tip, or to orient uniformly the magnetic axes of ferromagnetic nanoparticles.

[0012] The present invention relates to the general process of affixing nanoparticles to the tip of a scanning probe microscope, and need not be limited to magnetic nanocrystals. Nanoparticles comprised of magneto-optic, ferroelectric, piezoelectric, superconducting, semiconducting, magnetically-doped semiconducting, insulating, fluorescent, or chemically catalytic materials may be affixed to SPM tips in the manner described herewith.

[0013] The method of forming the scanning probe microscope tip comprises coating a scanning probe microscope tip with an adhesion promoter; dipping the tip through a layer of nanoparticles floating on a liquid subphase; and withdrawing the tip from the liquid subphase. Other methods of forming the scanning probe microscope tip include inking an elastomeric stamp with nanoparticles on it, and sticking the microscope tip into the elastomer; submerging the tip

into a solution of dispersed nanoparticles, and using electrostatic and electrochemical methods to attach the nanoparticles to the tip; and finally using lithographic techniques to attach the nanoparticles to the tip. After the nanoparticles have been affixed to the tip, chemical and physical treatments may be applied to the tip to impart to it desired properties. Heat, laser light, or a beam of electrons may be applied to the tip to strengthen the adhesion between the nanoparticles and the tip.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The foregoing and other objects, aspects and advantages will be better understood from the following detailed description of the preferred embodiments of the invention with reference to the drawings, in which:

[0015] Figure 1(a) is a schematic diagram of a method of coating an SPM tip;

[0016] Figure 1(b) is a schematic diagram of a method of coating an SPM tip;

[0017] Figure 1(c) is a schematic diagram of a method of coating an SPM tip;

[0018] Figure 2(a) is a schematic diagram of an SPM tip structure;

[0019] Figure 2(b) is a schematic diagram of an SPM tip structure;

[0020] Figure 2(c) is a schematic diagram of an SPM tip structure;

[0021] Figure 2(d) is a schematic diagram of an SPM tip structure;

[0022] Figure 2(e) is a schematic diagram of an SPM tip structure,

[0023] Figure 2(f) is a schematic diagram of an SPM tip structure; and

[0024] Figure 2(g) is a schematic diagram of a nanoparticle structure.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS OF THE INVENTION

[0025] As mentioned above, there is a need for a scanning probe microscope with improved spatial resolution. In order to increase the spatial resolution, the invention forms the microscope probe tip using chemically synthesized nanoparticles. The advantage conferred by a tip coated with chemically synthesized nanoparticles is that the region on the tip that interacts with the substrate is limited to a few nanoparticles. For a tip coated with magnetic nanoparticles, this region is much smaller than the interaction-region on MFM tips fabricated by conventional processes The smaller interaction-region leads to higher spatial resolution.

[0026] In a preferred embodiment of the present invention, the process of coating the tip is shown in sequence in Figures 1(a), 1(b), and 1(c). Figure 1 is not drawn to scale; wherein nanoparticles have a typical diameter of 2 nm - 20nm; the tip apex has a typical diameter of 20 nm - 50 nm; and the tip has a typical height of 10 μm - 30 μm. A nonmagnetic silicon AFM tip 1 is shown attached to a cantilever 10. The tip 1 is coated with a molecular layer of an adhesion-promoting chemical, n-(2-aminoethyl) 3-aminopropyl-trimethoxysilane, by dipping the tip into n-(2-aminoethyl) 3-aminopropyl-trimethoxysilane and then rinsing off the excess n-(2-aminoethyl) 3-aminopropyl-trimethoxysilane with ethanol. Other adhesion layers include polyethylineimine, polymethylmethacrylate, epoxy, cyanoacrylate adhesive, and an α,ω alkyl chain, wherein each functional group is selected from one of an amine, carboxylic acid, isocyanide, nitrile, phosphene, phosphonic acid, sulfonic acid, thiol, and trichlorosilane. The nanoparticles 2 are comprised of 8 nm-diameter grains of cobalt, coated with a single molecular layer of oleic

acid. The variability in the diameter of the nanoparticles 2 is less than 5%. A two-dimensional layer of magnetic nanoparticles 2, supported on a water subphase 40, is formed via a Langmuir-Blodgett (LB) technique, whereby a drop of solvent (e g., hexane) containing nanoparticles is deposited onto the surface of the water subphase 40. After the solvent evaporates, surface tension confines a two-dimensional layer of nanoparticles 2 to the water-air interface. A moveable barrier compresses the layer to form a closely-packed, ordered monolayer of nanoparticles 2. The tip 1 is dipped through the nanoparticles 2 into the water 40. Upon removal of the tip 1 from the water 40, some of the nanoparticles 2 attach themselves to the tip 1. The preferred embodiment described above can be varied in a number of obvious ways to create useful SPM tips.

[0027] The tip 1 need not be for MFM, but may also be for AFM, STM, SECM, NSOM, or for any other SPM technique The tip 1, or alternatively just the apex 5 of the tip 1, may be coated with any of a wide range of adhesion-promoters prior to the deposition of nanoparticles 2 onto the tip 1. Possible adhesion promoters include: n-(2-aminoethyl) 3-aminopropyl-trimethoxysilane, polyethylineimine, carboxylate-terminated trichlorosilane self-assembled monolayers, thin coatings of photo-cured adhesives, epoxies, and cyancrylate adhesives.

[0028] The tip 1 may be coated with a large variety of nanoparticles 2 that have been designed to have a useful property. Useful properties include, but are not limited to: ferromagnetism, paramagnetism, superparamagnetism, antiferromagnetism, ferrimagnetism, magneto optic response, ferroelectric effects, piezoelectric effects, superconductivity, semiconductivity, magnetically-doped semiconductivity, electrical insulation, fluorescence, and

chemical catalysis. In addition, the nanoparticle itself may be a composite material comprising materials with different properties.

[0029] The nanoparticles 2 can have precisely-controlled sizes ranging from as small as 2 nm up to 20 nm, depending on the application. Well-established chemical syntheses allow the creation of nanoparticles where the variability in the diameter of the nanoparticles is less than 15% of their diameter, and preferably less than 10% of their diameter. Preferably, the present invention uses nanoparticles 2 with a variability less than 5% of their diameter.

[0030] Furthermore, any of a large class of organic coats may be applied to the nanoparticles to produce a coating with a thickness between 0.5 nm and 5 nm. The organic coat comprises one or more types of molecules, where each molecule contains a head-group that binds to the nanoparticle and a tail-group that extends away from the nanoparticle. The head-group may be selected from one of an amine, carboxylic acid, isocyanide, nitrile, phosphene, phosphonic acid, sulfonic acid, thiol, and trichlorosilane. The tail-group may be selected from one of an alkyl chain, aryl chain, fluorocarbon, siloxane, fluorophore, DNA, carbohydrate, and protein.

[0031] As illustrated in Figure 2(c) a mixed coating comprised of nanoparticles 2, 4 with two or more compositions, sizes, or organic coatings may be formed. Either a mixed layer of nanoparticles 2, 4 is deposited on the subphase, or the tip is processed two or more times to deposit multiple layers of different types of nanoparticles 2, 4. Figure 2(a) shows an adhesion promoter 6 deposited on the entire tip 1, including the tip apex 5. Moreover, Figure 2(g) illustrates a single nanoparticle 2 with an organic coating 3 encapsulating the nanoparticle 2.

[0032] Nanoparticles 2 may be deposited over the entire tip 1 in one layer as in Figure 2(d) or in multiple layers as in Figure 2(b). Alternatively, nanoparticles 2 may be deposited only

over the apex 5 of the tip 1 in order to achieve higher spatial resolution, as in Figure 2(e). Alternatively, just a single nanoparticle 2 may be deposited on the apex 5 of the tip 1, as in Figure 2(f).

[0033] After the deposition of nanoparticles 2, the tip 1 may be treated to promote the adhesion of nanoparticles 2 to the tip. Possible post-deposition treatments include exposure to ultraviolet light, intense coherent light, or a beam of electrons.

[0034] Alternatively, the nanoparticles 2 may be annealed at a high temperature. In addition to promoting adhesion of the nanoparticles 2 to the tip 1, the annealing step may be used to fuse the nanoparticles 2 into an electrically-continuous film. Furthermore, a magnetic field may be applied to ferromagnetic nanoparticles 2 during an annealing step to orient uniformly the magnetic axes of all the nanoparticles 2. For ferroelectric nanoparticles, an electric field may be applied during an annealing step to orient uniformly the electric polarization axes of all the nanoparticles

[0035] The tip 1 can be fabricated using several alternative approaches. In a first approach, the tip 1 is dipped onto a liquid subphase 40. In this technique single-layer films of nanoparticles can be formed by depositing a drop of spreading solvent (e g. hexane, toluene, heptane, pentane, chloroform, dichloromethane) containing nanoparticles onto the surface of a liquid subphase. The liquid subphase may be water, ethylene glycol, propylene glycol, or mixtures thereof. Surfactants such as sodium octanesulfonate may be added to the subphase to improve the uniformity of the layer of nanoparticles. After the solvent evaporates, surface tension confines the nanoparticles to the subphase-air interface, resulting in a two-dimensional film results. Using standard LB techniques, the film can be compressed to form a closely-packed, ordered monolayer

film of nanoparticles. Dipping the tip into the liquid subphase, and then retracting it, causes the nanoparticle monolayer to be transferred onto the tip. Furthermore, dipping the tip in this method is done such that the tip is not fully submerged into the liquid solution, rather it is dipped into the upper floating monolayer of nanoparticles, which are floating on the liquid solution.

[0036] Dipping the tip 1 has the potential to coat the entire tip 1 with nanoparticles 2. This may be adequate for some applications as will be addressed. Furthermore, dipping in this manner makes the process easy scalable, such that an entire wafer of SPM tips may be dipped in one step.

[0037] The second approach provides for dipping a flat sheet of an elastomer (such as polydimethylsiloxane (PDMS)) into a liquid subphase 40 on which floats a layer of nanoparticles, such that a monolayer of nanoparticles adheres to the surface of the elastomer. The tip 1 is then brought into contact with a region of the elastomer that has been coated with nanoparticles and the nanoparticles transfer from the elastomer to the tip. This method allows for better control of the dip depth than can be achieved by dipping the tip directly into the liquid subphase, and the possibility of mounting a single nanoparticle 2 on the tip 1. Using this method, it is possible to use a laser beam to monitor the tip-elastomer separation, and therefore control very precisely the dip depth of SPM tip into the elastomer.

[0038] However, this need for monitoring the precise position of the tip also makes it more difficult to parallelize than by direct deposition from the liquid subphase 40. Although more precise, this approach requires careful monitoring of each individual tip coating. It is therefore not amenable to batch processing of many tips in parallel

[0039] The third method allows for dipping the tip 1 onto a monolayer of nanoparticles floating on a thin liquid layer comprised of a nonvolatile liquid, such as ethylene glycol, propylene glycol, photoresist, or paraffin. This method has the advantage of dipping into a liquid subphase that is easy to remove from the tip 1 after the deposition of nanoparticles is complete.

[0040] The third method is essentially a combination of dipping directly from a liquid subphase (method 1) and coating from an elastomer (method 2). By creating a nanoparticle monolayer on a liquid subphase (similar to method 1) that is extremely thin, it is possible to use the laser-based techniques of method 2 to control the depth to which the tip is dipped into the nanoparticles. In addition, by dipping the tip into liquid it is possible to minimize the damage to the SPM tip by bringing it into contact with solids (elastomers, in method 2).

[0041] Also, the surface tension may limit the minimum area on the tip 1 that is coated with nanoparticles 2. If the liquid wets the tip, then capillary action will draw the liquid and the nanoparticles up the tip When the tip is withdrawn, it will be coated with nanoparticles wherever the liquid contacted it.

[0042] In the fourth method, the tip 1 is dipped (submerged) into a thin layer of a solution of the nanoparticles in a nonvolatile solvent. Nanoparticles randomly diffusing in the solvent will come into contact with the tip. Provided that the nanoparticles stick to the tip, a monolayer of particles will form on the tip. Then, the solvent is washed off. The fourth method has the advantage over the third method in that it is not necessary to form a closely-packed monolayer of nanoparticles on the surface of the liquid; a possibly challenging task.

[0043] Once again, the surface tension may limit the minimum area on the tip 1 that is coated with nanoparticles 2. As in the third approach, the wetting behavior of the liquid on the tip may affect the extent to which the tip is coated with nanoparticles.

[0044] In a fifth method, an electric potential is applied to the tip 1 in an electrochemical solution of nanoparticles (with a supporting electrolyte). Electric fields emanating from the tip may attract nanoparticles and cause them to stick to the apex of the tip 1. The electrochemical solution comprises nanoparticles, a solvent, and an electrode held at a neutral potential. Furthermore, the electrochemical solution comprises a supporting electrolyte and a reference electrode.

[0045] A sixth method involves performing a variant of the "liftoff" technique used in semiconductor processing on the tip 1. The entire tip 1 is coated with a soft sacrificial layer Possible materials for the sacrificial layer are: photoresist, paraffin, or nail polish. Then the tip 1 is scanned in contact against a hard substrate to abrade and remove the sacrificial layer from the apex 5. Thus, all but the apex 5 of the tip 1 is coated with a sacrificial layer. Nanoparticles 2 are deposited over the apex 5 and the sacrificial layer, and then the sacrificial layer is removed The liftoff process leaves nanoparticles 2 only at the apex 5.

[0046] In all of the above approaches, the scanning probe microscope tip can be treated after deposition of the nanoparticles through heat treatment, exposure to ultraviolet light, exposure to an electron-beam, or exposure to a laser light. In the heat treatment process, the tip can be heated to melt the nanoparticles to form a continuous film, or alternatively, the tip can be heat treated to form an alloy from a heterogeneous nanoparticle coating. Similarly, the tip can be heat treated in a magnetic field to orient uniformly the magnetic moments of ferromagnetic

nanoparticles, or the tip can be heat treated to cause a chemical reaction between heterogeneous nanoparticles.

[0047] There are several applications which can employ scanning probe tips that have been coated with nanoparticles. First, in magnetics, the present invention aids in performing magnetic force microscopy (MFM). To achieve high resolution, an MFM tip should maximize the amount of magnetic material near the specimen and minimize the amount of magnetic material far from the specimen. This goal is achieved in an MFM tip with a single nanoparticle at the apex, similar to the illustration in Figure 2(f). The nanoparticles may be either ferromagnetic or superparamagnetic. Also, MFM may be performed with a coating of ferromagnetic or superparamagnetic nanoparticles that extends up the tip as shown in Figures 2(c), 2(d) and 2(e). This extended coating is easier to make than a single-nanoparticle tip because it does not require fine control over the deposition process, and yet still provides higher resolution than does a solid conical tip.

[0048] A tip coated with one or more ferromagnetic nanoparticles may be annealed in the presence of a magnetic field at a temperature above the Curie temperature, to align the magnetic axes of the nanoparticles. Superparamagnetic or uniformly oriented ferromagnetic nanoparticles are superior to MFM with a solid magnetic tip because the number of interacting spins grows only linearly with the tip radius as one extends away from the specimen In a solid conical tip, the number of interacting spins grows proportionally to the square of the tip radius. A tip coated with randomly oriented (un-annealed) ferromagnetic nanoparticles may provide higher resolution than an annealed tip. The magnetic forces on nanoparticles far from the apex will average to zero because each nanoparticle may be associated with an oppositely oriented nanoparticle at the same

distance from the sample. Only the forces on those nanoparticle(s) at the apex will remain unbalanced.

[0049] In a second application, the invention is used in scanning tunneling spectroscopy, wherein a metallic nanoparticle is mounted on a conductive tip and a tunneling current passes from the tip through the nanoparticle to the specimen. Electrons passing through the nanoparticle will not have the continuous distribution of energy levels that are found in a bulk metal. Rather, the electronic energies will be restricted to discrete values. The dependence of the current through the nanoparticle on the potential applied to the nanoparticle will provide information on the electronic band-structure of the specimen immediately under the nanoparticle. This information is difficult to obtain with a tip that has not been coated with nanoparticles.

[0050] In a third application, fluorescent nanoparticles are placed on a silicon tip. Then, the tip is illuminated with ultraviolet light and the fluorescence from the nanoparticles is detected as the tip is scanned over a specimen. The nanoparticles act as a light source with an aperture size equal to the diameter of a nanoparticle, which is far below the wavelength of light emitted by the nanoparticles. The fluorescent light can be used in the near-field to create optical images of the specimen with a resolution in the order of the diameter of a nanoparticle. Furthermore, a measurement of nonradiative energy transfer from the nanoparticle to the specimen will provide information about optically active compounds on the surface of the specimen In the above application the silicon tip may be replaced by a sharpened optical fiber, of the sort used in near-field scanning optical microscopy (NSOM), and one or both of the exciting UV light and the fluorescent light may pass through the fiber.

[0051] Fourth, in magneto-optics, the invention is useful for imaging magnetic fields if a tip (Si or NSOM) is coated with nanoparticles with strong magneto-optical properties. The tip is scanned over a specimen while the relevant magneto-optical property of the nanoparticle(s) on the tip is measured. Some possible coatings are: materials with large magneto-optic rotation (such as yttrium-iron-garnet, YIG), magnetically-doped fluorescent semiconductors, heterogeneous superlattices of magnetic and nonmagnetic fluorescent nanoparticles (rate of nonradiative energy transfer will depend on the field), and heterogeneous superlattices of magnetic and nonmagnetic metals (degree of electronic delocalization, and hence reflectivity, will depend on the field).

[0052] A fifth application of the invention is in catalysis, wherein a catalytically active nanoparticle is mounted on the tip. In a proper chemical environment this nanoparticle is used to localize a reaction to a very small volume This is useful for high-resolution chemical modification of surfaces or in single-molecule studies.

[0053] While the invention has been described in terms of preferred embodiments, those skilled in the art will recognize that the invention can be practiced with modification within the spirit and scope of the appended claims.